Electronic Structure of Two-Dimensional Crystals of Hexagonal Boron Nitride

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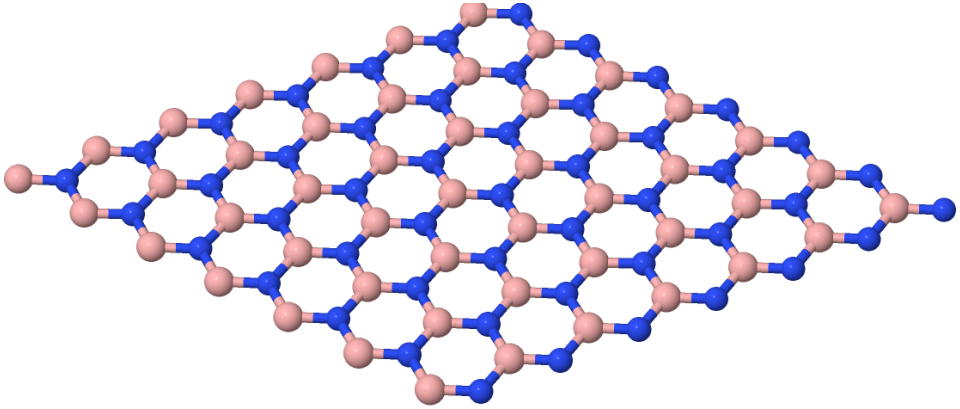
Introduction: Hexagonal Boron Nitride (I)

- H-BN: B and N atoms occupy the A and B sublattices of a 2D honeycomb lattice.
  - Atomic structure and lattice parameter are similar to graphene.
  - However, whereas pristine graphene is a gapless semiconductor, h-BN is an insulator because the sublattice symmetry is broken.

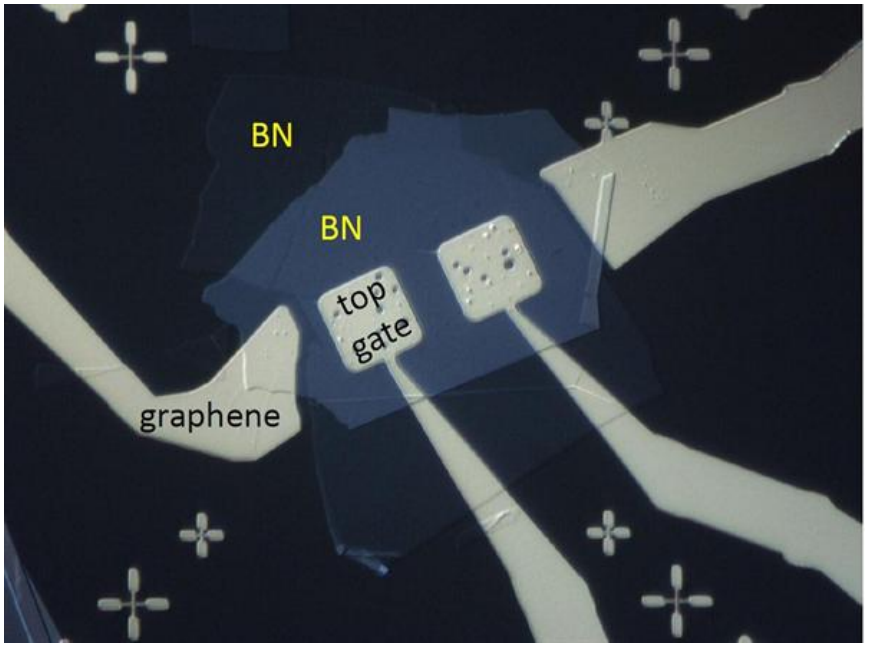


- Bulk h-BN (a.k.a. *white graphite*): BN layers are weakly bound together (mainly) by van der Waals interactions.
  - Gives rise to lubricating properties.
  - Possible to produce monolayers of BN by mechanical exfoliation.

- Stacking arrangement of bulk h-BN: AA'.
  Each $B^{\delta+}$ ion has an $N^{\delta-}$ vertically above it and *vice versa*.

Introduction: Hexagonal Boron Nitride (II)

- **H-BN is the best substrate for graphene-based electronics**:
  - the surfaces may be atomically smooth;
  - it is a very good insulator; and
  - it has a similar lattice parameter to graphene.



- Atomically flat BN is also a potentially important component in novel electronic devices based on 2D materials, e.g., high-speed transistors and supercapacitors.

- To date, experimentalists have not succeeded in measuring the optoelectronic properties of monolayer BN. Our knowledge of these properties is based on:
  - extrapolation from experimental results for thin films (dozens of layers); and
  - density functional theory (DFT) calculations.

Electronic Properties of Hexagonal Boron Nitride

- Key optoelectronic property: nature (direct or indirect) and magnitude of the **electronic band gap**.

- Challenges for theory:
  - Experimental results are currently unavailable.
  - DFT is not reliable for determining band gaps.
  - Bulk h-BN exhibits a large exciton binding energy. Estimates range from 0.149 eV (experiment plus Wannier model) to 0.72 eV (GW-Bethe–Salpeter equation). Exciton binding is enhanced in the monolayer.
  - **2D systems exhibit unpleasant finite-size effects**.

- We have therefore used quantum Monte Carlo (QMC) methods as implemented in CASINO to investigate the band structure and excitonic effects in h-BN.
  - We use variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC).
  - First QMC calculations of the band structure of 2D materials?

- We have investigated the effects of lattice dynamics on the band gap within DFT.

DFT Calculations (Relaxation, Lattice Dynamics, Band Structure)

- Parameters for our DFT (CASTEP) calculations:
  - Exchange-correlation functionals used: LDA, PBE and hybrid HSE06.
  - Artificial periodicity: 40 a.u.
  - 53×53 $\mathbf{k}$-point grid in LDA and PBE band-structure calculations; 29×29 $\mathbf{k}$-point grid in lattice-dynamics calculations; 11×11 $\mathbf{k}$-point grid in HSE06 calculations
  - Plane-wave cutoff: 25 a.u. in calculations with ultrasoft pseudopotentials; 30 a.u. in (HSE06) calculations with norm-conserving pseudopotentials.
  - Finite displacements to evaluate force constants: 0.08 a.u.

- Replacing ultrasoft with norm-conserving pseudopotentials changed the DFT-PBE $K \to \Gamma$ and $K \to K$ gaps from 4.69 to 4.76 eV and 4.67 to 4.79 eV, respectively.
  - Uncertainty in gap due to pseudopotential: ~ 0.1 eV. *Small, but makes the difference between predicting direct and indirect gaps.*
  - Dirac-Fock pseudopotentials used in our QMC calculations give similar DFT gaps to the norm-conserving pseudopotentials.
  - DFT-PBE lattice parameter changes from 2.512 to 2.487 Å when the ultrasoft pseudopotential is replaced by a norm-conserving pseudopotential.

Nuclear Contribution to the Band Gap (I)

- Born–Oppenheimer approximation: electronic wave functions and energies depend parametrically on nuclear positions; electronic total energy acts as a potential in which the nuclei move.
  - When an electron is excited, the B.–O. potential surface abruptly changes.
  - Suppose we are at zero temperature, so all phonon modes are in their ground state.
  - Nuclear contribution to total energy: zero-point energy (ZPE) of phonon modes.
  - Provided the overlap between the ground-state nuclear wave functions in the electronic ground state and excited state is non-negligible, the phonon-renormalised gap is the difference between the total energy including phonon ZPE in the ground state and the total energy including ZPE in the electronic excited state.

- To calculate the nuclear zero-point energy (ZPE) contribution to the band gap:
  - *Perform DFT lattice dynamics calculation in the electronic ground state.*
  - *Perform DFT lattice dynamics calculation in the electronic excited state.*
  - *Difference in ZPEs gives nuclear correction to band gap at zero temperature.*

Nuclear Contribution to the Band Gap (II)

- We used the method of finite displacements in a 3×3 supercell and with an $n \times n$ $\mathbf{k}$-point grid in the supercell, including Γ.

- For the electronic excited state, we swapped the occupancies of the ground-state highest occupied and lowest unoccupied band.

- Taking the difference of the total ZPEs in the $3n \times 3n$ supercell corresponding to the unfolded $\mathbf{k}$ points gives the phonon contribution to the electronic excitation energy.

- The promotion of the electron from the highest occupied to the lowest unoccupied band at Γ in the 3×3 supercell corresponds to a promotion at K in the Brillouin zone of the primitive cell; thus the phonon contribution to the gap calculated above is the correction to the $K \rightarrow K$ gap.

- Assume the phonon corrections for $K \rightarrow \Gamma$ are similar.

- The calculations used norm-conserving DFT pseudopotentials, the PBE exchange-correlation functional, a plane-wave cutoff energy of 40 a.u. and finite displacements of 0.08 a.u.

Evaluating Quasiparticle and Excitonic Gaps in QMC (I)

- To calculate excitation energies using QMC: take **differences of total energies** obtained with trial wave functions that correspond to the ground state or an excited state.
  - Exploits the fixed-node approximation.
  - Choose orbital occupancy to get appropriate excited-state wave functions.

- Quasiparticle bands for unoccupied states: $\mathcal{E}_i(\mathbf{k}) = E^+(\mathbf{k}, i) - E^{\mathrm{GS}}$, where $E^+(\mathbf{k}, i)$ is the total energy when an electron is added to band i at $\mathbf{k}$ and E^{GS} is the ground-state energy.

- Quasiparticle bands for occupied states: $\mathcal{E}_i(\mathbf{k}) = E^{\mathrm{GS}} - E^-(\mathbf{k}, i)$, where $E^-(\mathbf{k}, i)$ is the total energy when an electron is removed from band i at $\mathbf{k}$.

- Quasiparticle band gap: difference of the energy bands at conduction-band minimum (CBM) and valence-band maximum (VBM):

$$\Delta_{\mathrm{qp}} = \mathcal{E}_{\mathrm{CBM}} - \mathcal{E}_{\mathrm{VBM}} = E^+_{\mathrm{CBM}} + E^-_{\mathrm{VBM}} - 2E^{\mathrm{GS}}.$$

Evaluating Quasiparticle and Excitonic Gaps in QMC (II)

- Excitonic gap: energy difference when an electron is promoted from VBM to CBM:

$$\Delta_{\mathrm{ex}} = E^{\mathrm{pr}}_{\mathrm{VBM}\to\mathrm{CBM}} - E^{\mathrm{GS}},$$

  where $E^{\mathrm{pr}}_{\mathrm{VBM}\to\mathrm{CBM}}$ is the total energy evaluated with a trial wave function in which the VBM orbital has been replaced by the CBM.

- DMC retrieves a large but finite fraction of the correlation energy.
  - Hartree–Fock theory: band gaps are significantly overestimated.
  - Assume the fraction of correlation energy retrieved in the ground state is similar to the excited state: the DMC gaps are upper bounds.
  - If we increase the fraction of correlation energy retrieved, e.g., by including a backflow transformation, we expect to see a decrease in the energy gap.

DMC for Excited States

- DMC for the lowest-energy eigenfunction that has the same symmetry as the trial wave function, provided that the trial wave function transforms as a 1D irreducible representation of the symmetry group of the Hamiltonian:
  - Variational principle for DMC energy: fixed-node error in energy is (i) positive and (ii) second order in the error in the nodal surface.
  - Zero-variance principle: if trial wave function is exact, all local energies are equal to the energy eigenvalue.

- DMC for a general excited state:
  - No variational principle: fixed-node error can be either positive or negative. Error is first order in the error in the nodal surface.
  - Energy expectation with a Slater(–Jastrow(–backflow)) trial wave function constructed using an appropriate set of orbitals will exceed the excited-state energy. Hence we expect the fixed-node error will be positive in general.
  - Still have zero-variance principle.

- So DMC "works" for excited states.

Trial Wave Functions, Etc. (I)

- We used Slater-Jastrow (SJ) wave functions:
  - DFT-PBE orbitals from CASTEP were re-represented in blips (i) to improve the scaling and (ii) to discard the artificial periodicity in the out-of-plane direction.
  - Jastrow factor: electron–electron (isotropic polynomial plus 2D plane wave expansion), electron–ion and electron–electron–ion terms were optimised by unreweighted variance minimisation.
  - Bitter experience: wave functions optimised by unreweighted variance minimisation are less likely to result in population explosions in DMC than wave functions optimised by energy minimisation.

- All DMC gaps have been linearly extrapolated to zero time step (using time steps of 0.01 and 0.04 a.u.).

- We used the ground-state Jastrow factor (and backflow function) in excited states.
  - Fixed-node DMC energy does not depend on the Jastrow factor.
  - Relaxation of backflow in an excited state is a manifestation of finite-size error.

Trial Wave Functions, Etc. (II)

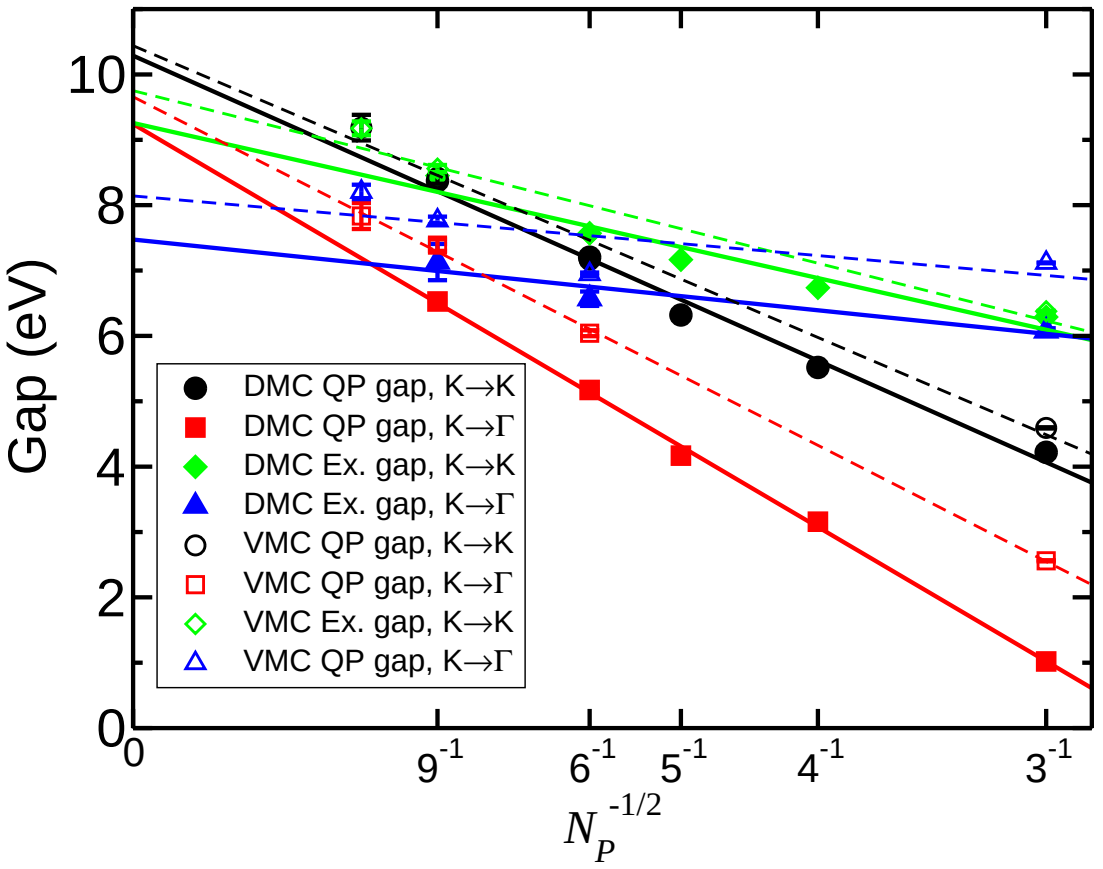
- We performed test calculations with Slater-Jastrow-backflow wave functions:
  - SJB wave functions were optimised by energy minimisation.
  - Backflow reduces the DMC gaps by a small amount [$0.10(3)$ eV on average].
  - VMC and DMC results in a 3×3 cell:

Method	E^{GS} (eV/p. cell)	σ^2_{GS} (a.u.)	QP gap (eV) $K \to \Gamma$	QP gap (eV) $K \to K$	Exc. gap (eV) $K \to \Gamma$	Exc. gap (eV) $K \to K$
HFVMC	$-341.961(4)$	21.39	$2.63(8)$	$5.95(8)$	$7.13(5)$	$7.65(5)$
SJ-VMC	$-349.8780(4)$	3.18	$2.559(9)$	$4.593(9)$	$7.118(6)$	$6.378(5)$
SJB-VMC	$-350.229(2)$	2.11	$2.55(4)$	$4.46(4)$	$7.18(2)$	$6.30(2)$
SJ-DMC	$-350.747(4)$	N/A	$1.02(9)$	$4.22(8)$	$6.08(4)$	$6.29(4)$
SJB-DMC	$-350.857(2)$	N/A	$0.86(4)$	$4.09(4)$	$6.04(2)$	$6.22(2)$

- The fraction of SJB-DMC correlation energy retrieved at the SJ-VMC or SJB-VMC level is much smaller for excited states than the ground state.
  - Undermines our assumption that the quality of our calculations is similar in the ground state and excited state.

Comparison of VMC and DMC Gap Results

- VMC is cheaper than DMC, by a factor of more than 50.
- Whereas fixed-node DMC total energies (and hence gaps) are independent of the Jastrow factor, this is not true of VMC.
- Nevertheless, any effect of not reoptimising the Jastrow factor in excited states is a form of finite-size error.



- The VMC gaps are generally larger than the DMC gaps, as expected.
- Although the VMC and DMC gaps show the same finite-size behaviour, the VMC results cannot be used to extrapolate the DMC gaps to the thermodynamic limit, even though VMC results can be obtained for substantially larger system sizes.

Singlet and Triplet Excitonic States

- We have calculated the SJ-DMC energy differences between the singlet and triplet excitonic states in 3×3 supercells of BN.
- We used single-determinant trial wave functions in which an electron was promoted without and with a spin-flip.
- We used the set of orbitals obtained in a non-spin-polarised ground-state DFT-PBE calculation together with the Jastrow factor optimised in the ground state.
- The singlet excitonic state for a promotion from $K \rightarrow K$ is 0.12(2) eV lower in energy than the triplet state.
- For $K \rightarrow \Gamma$, the triplet excitonic state is lower in energy by 0.02(2) eV (insignificant).
- Apart from these tests, all the calculations reported in this article were performed using singlet excitonic states.

Finite-Size Effects (I)

- Although the asymptotic behaviour of the ground-state energy as a function of system size in a 2D-periodic system is known, the asymptotic form of the finite-size error in the band gaps is unknown.

- We used a range of simulation cell sizes, from 2×2 to 9×9 primitive cells.

- Different choices of simulation-cell Bloch vector $\mathbf{k}_s$ allow one to obtain different points on the band structure in a finite cell:
  - For a $3n \times 3n$ supercell with $\mathbf{k}_s = \mathbf{0}$, the orbitals include bands at both Γ and K. One can make additions or subtractions at Γ or K and promote electrons either from K to Γ or from K to K.
  - Otherwise, one can choose $\mathbf{k}_s$ so that the orbitals at Γ are present, or the orbitals at K, but not both.
  - Hence it is only possible to calculate the $K \rightarrow \Gamma$ excitonic gap in $3n \times 3n$ supercells.
  - The quasiparticle gap from $K \rightarrow \Gamma$ can always be calculated for a given supercell size by determining the CBM and VBM using two different values of $\mathbf{k}_s$.

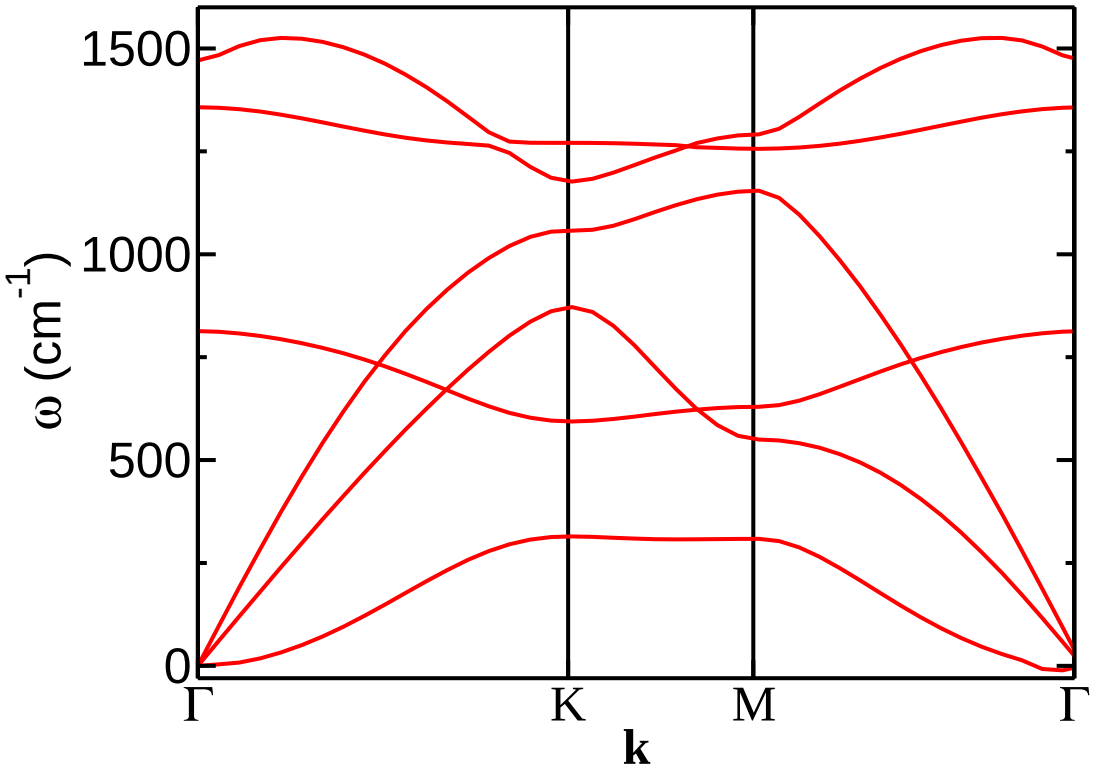
Finite-Size Effects (II)

- In these preliminary results we have **assumed** the finite-size error is inversely proportional to the linear size of the cell.
  - This is a plausible finite-size scaling that is not obviously inconsistent with the results shown in the figure.
  - To-do: work out what the scaling ought to be. **Answers on a postcard, please.**

- It is likely that the excitonic gap will behave differently as a function of system size once the linear size of the simulation cell exceeds the exciton Bohr diameter.
  - When the simulation cell is small, the exciton is artificially compressed, leading to an overestimate of the binding energy.

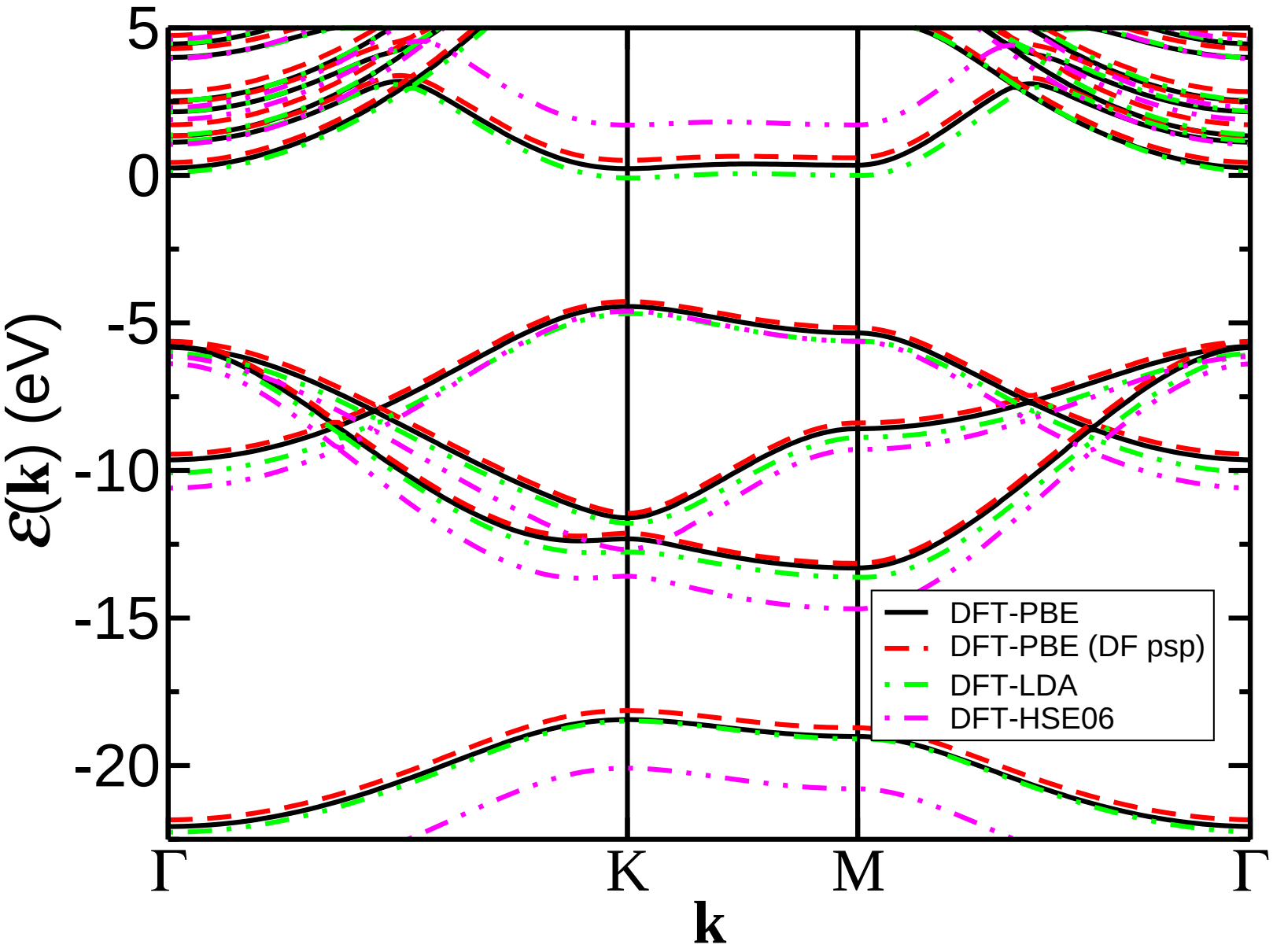
Results: Lattice Parameter and Dynamical Stability (I)

Method	Lattice parameter (Å)
DFT-LDA	2.491
DFT-PBE	2.512
DFT-HSE06	2.45
Exp. (bulk)	2.5040



- We used the DFT-PBE lattice parameter in all our QMC calculations.
- Phonon dispersion curve was obtained using DFPT.
  - LO branch ought to go linearly to TO frequency at Γ; the fact that it does not is due to the artificial periodicity.
- There is a small (spurious) region of dynamical instability at Γ, which depends on plane-wave cutoff, $\mathbf{k}$-point sampling, etc.

Results: DFT Band Structures



Results: Band Effective Masses (I)

- We fitted

$$\mathcal{E}(\mathbf{k}) = \mathcal{E}_0 \pm \frac{k^2}{2m} + Ak^4 + Bk^6 + Ck^6\cos(6\theta) + Dk^3\cos(3\theta) + Ek^5\cos(3\theta),$$

  to the valence and conduction bands within a circle of radius 10% of the Γ–M distance around the K point, where $\mathbf{k}$ is the wavevector relative to the K point.

  – The root-mean-square residual over this area is less than 0.3 meV in each case.

- We fitted

$$\mathcal{E}(\mathbf{k}) = \mathcal{E}_0 \pm \frac{k^2}{2m} + Ak^4 + Bk^6 + Ck^6\cos(6\theta),$$

  to the conduction band within a circle of radius 40% of the Γ–M distance about Γ.

  – RMS residual over this area is less than 0.3 meV.
  – It is clearly much easier to represent the band over a large area around Γ than K.

- The band edge and effective mass are unchanged when the radius of the region used for the fit is reduced.

Results: Band Effective Masses (II)

Method	Band	Location	$\mathcal{E}_0$	m
DFT-LDA	Cond.	Γ	0.00397	0.96
DFT-LDA	Cond.	K	-0.00327	0.89
DFT-LDA	Val.	K	-0.172	0.61
DFT-PBE	Cond.	Γ	0.00919	0.95
DFT-PBE	Cond.	K	0.00838	0.90
DFT-PBE	Val.	K	-0.163	0.63
DFT-HSE06	Cond.	Γ	0.0471	0.98
DFT-HSE06	Cond.	K	0.0711	1.07
DFT-HSE06	Val.	K	-0.161	0.63

Mott–Wannier Model of Excitonic Effects

- Mott–Wannier binding energy of an exciton in 2D: $E_{\mathrm{ex}} = -2\mu/\epsilon^2$, where $\mu = m_e m_h/(m_e + m_h)$ is the exciton reduced mass and m_e and m_h are the electron and hole masses, respectively.

- Corresponding exciton Bohr radius: $a_{\mathrm{ex}} = \epsilon/\mu$.

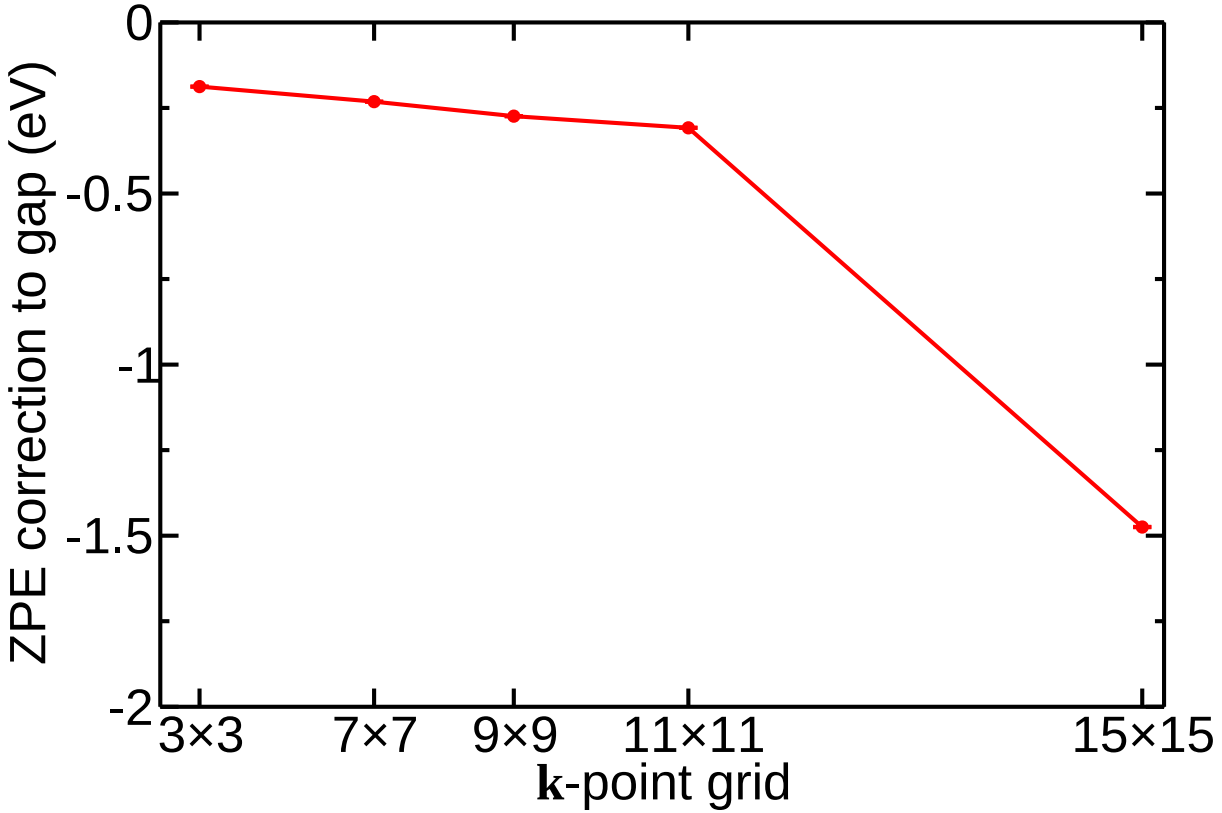
- Experimental static in-plane dielectric constant of bulk h-BN: $\epsilon = 6.85$. Assume the dielectric constant for monolayer BN to be similar.

Method	Excitation	Bohr rad. (Å)	Bind. en. (eV)
DFT-LDA	$K \to \Gamma$	9.74	-0.433
DFT-LDA	$K \to K$	10.0	-0.420
DFT-PBE	$K \to \Gamma$	9.58	-0.439
DFT-PBE	$K \to K$	9.79	-0.430
DFT-HSE06	$K \to \Gamma$	9.47	-0.445
DFT-HSE06	$K \to K$	9.15	-0.460

- Wigner–Seitz cell radius of largest supercell used (9×9): 9.26 Å.

Renormalisation of the Gap due to Electron–Phonon Coupling

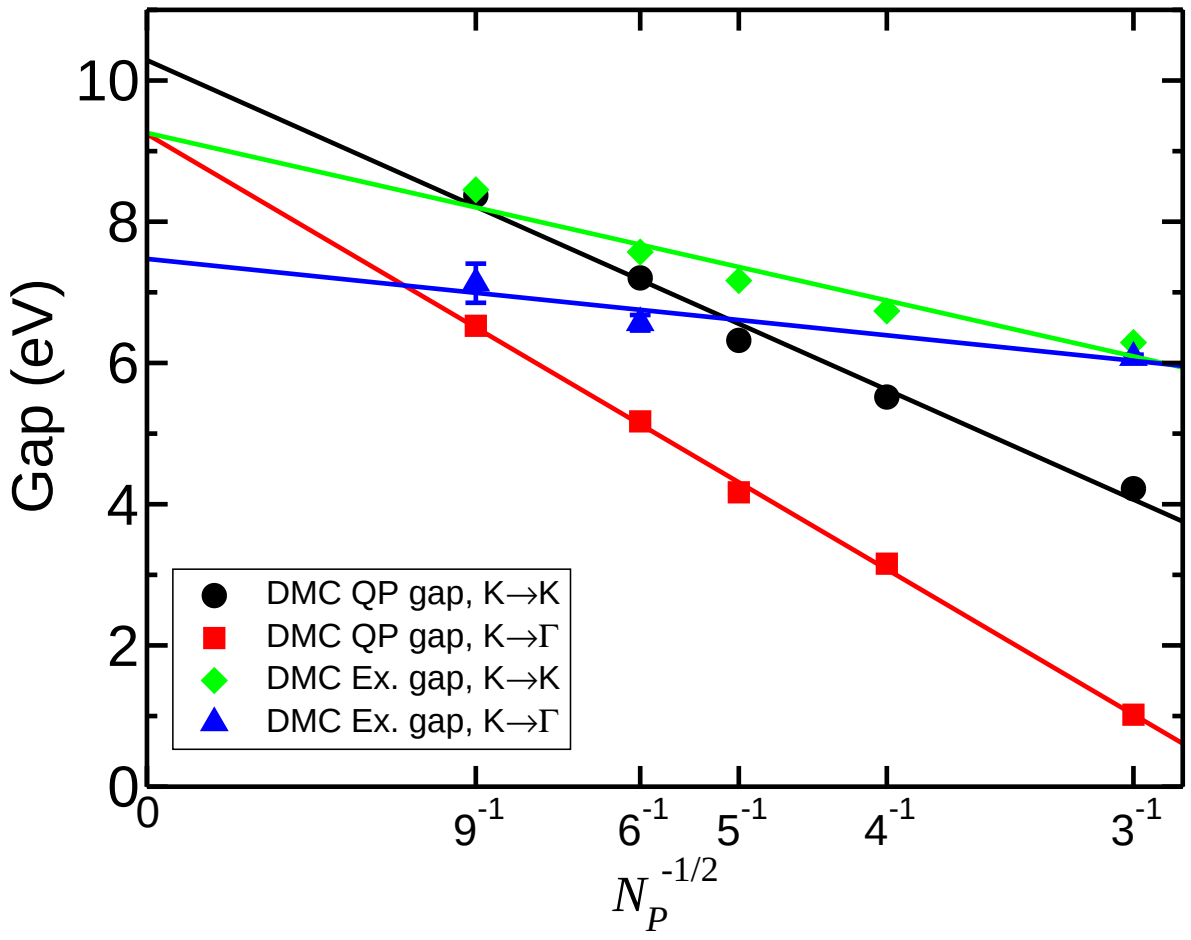
- Nuclear motion causes a small but significant reduction in the electronic band gap.
  - The gap renormalisation shows great sensitivity to the number of $\mathbf{k}$ points used in the 3×3 supercell. No real evidence of convergence.
  - Perhaps of the order -0.3 eV.
  - To-do: use the approach described by Bartomeu. Ought to agree. . .



Finite-Size Effects

- Finite-size extrapolation with guess at exponent. . .

- Excitons are unbound in small cells.
  - They are bound in the infinite system limit (as one would rather hope).
  - They become bound once the cell size becomes comparable with the estimated exciton Bohr diameter.



Energy-Gap Results

- We find the gap of monolayer BN to be **indirect** ($K \to \Gamma$) and about 7.2 eV.

- Experiment for single-crystal h-BN with around 15 layers: find a direct ($K \to K$) gap of 5.9 eV in single-crystal BN with around 15 layers.

Method	Quasiparticle gap (eV)		Excitonic gap (eV)	
	$K \to \Gamma$	$K \to K$	$K \to \Gamma$	$K \to K$
DFT-LDA	4.79	4.60	N/A	N/A
DFT-PBE	4.69	4.67	N/A	N/A
DFT-HSE06	5.65	6.31	N/A	N/A
GW	7.00	7.70	N/A	N/A
DMC	9.5(1)	10.4(2)	7.5(3)	8.7(3)

- In the thermodynamic limit the excitonic gaps lie below the quasiparticle gaps, as expected.

- The exciton binding is large: 1.7(4) eV for $K \to K$ and 2.0(3) eV for $K \to \Gamma$.

Conclusions

- We have performed DFT and QMC calculations to determine the electronic structure of monolayers of hexagonal BN, as an example of a 2D material.
- We find the QP gap to be indirect ($K \rightarrow \Gamma$) and of magnitude 9.5 eV.
- We find that monolayer BN exhibits a very large exciton binding energy of about 2 eV.
- Not much agreement between DFT, GW or QMC.

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